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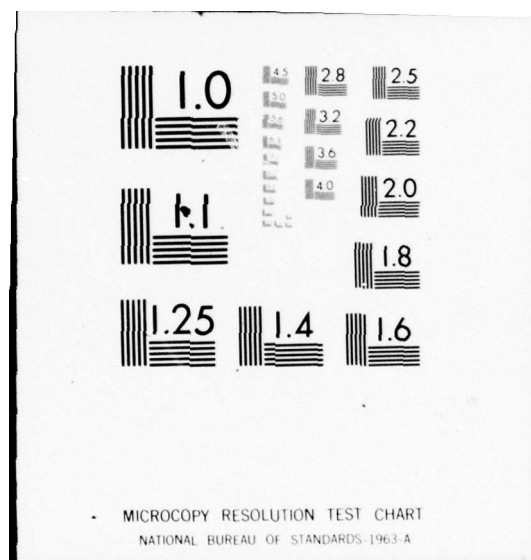OCT 77 A H GERBER, J R CABLE   N00014-75-C-0991
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OFFICE OF NAVAL RESEARCH

Contract N00014-75-C-0991

Project No. NR 356-604

FINAL REPORT

POLY(ORGANONITRILES)

by

Arthur H. Gerber
James R. Cable

HORIZONS RESEARCH INCORPORATED
23800 Mercantile Road
Cleveland, Ohio 44122

October 1977

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Preparation of poly(organonitriles) via a ring opening polymerization of triazine monomers is not a viable approach. A variety of substituted triazines were screened using metallic and nonmetallic catalysts at elevated temperatures.

Preparation of poly(organonitriles) via anionic polymerization of organic cyanates can be controlled to produce linear low

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molecular weight products. Aryl cyanates were easily synthesized whereas $CF_3CH_2OC{\equiv}N$ could not be satisfactorily prepared. Both cyanate and catalyst structures are important in determining product composition. Preferred systems comprise using a hindered aryl cyanate monomer and a hindered alkali aryloxide catalyst. The organic ligands of the resulting product can be easily exchanged with trifluoroethoxy groups by reaction with CF_3CH_2ONa.

ABSTRACT

Preparation of poly(organonitriles) via a ring opening polymerization of triazine monomers is not a viable approach. A variety of substituted triazines were screened using metallic and nonmetallic catalysts at elevated temperatures.

Preparation of poly(organonitriles) via anionic polymerization of organic cyanates can be controlled to produce linear low molecular weight products. Aryl cyanates were easily synthesized whereas $CF_3CH_2OC\equiv N$ could not be satisfactorily prepared. Both cyanate and catalyst structures are important in determining product composition. Preferred systems comprise using a hindered aryl cyanate monomer and a hindered alkali aryloxide catalyst. The organic ligands of the resulting product can be easily exchanged with trifluoroethoxy groups by reaction with CF_3CH_2ONa.

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POLY(ORGANONITRILES)

1.0 OBJECTIVES

Preparation of high molecular weight poly(organonitriles), $+(RO)C=N+_n$, where R may be selected from a variety of organic ligands. A secondary objective would comprise determining the effects of polymer structure on physical and chemical properties.

2.0 INTRODUCTION AND BACKGROUND

Poly(organonitriles) are of interest because they are potentially relatively inexpensive and should display excellent thermal and chemical resistance. Remarkable stability has been demonstrated by poly(benzonitrile) [Ref. 1]. Preparation and characterization of linear poly(organonitriles) of structures $+(R)C=N+_n$ and $+(RO)C=N+_n$ has been very limited to date and no preparation of high molecular weight species has been disclosed.

A variety of drastic (very high temperatures in the presence of large amounts of acidic catalyst) or impractical methods have been employed to prepare a very limited number of poly(organonitriles). These have included polymerization of a 2,4,6-trisubstituted-s-triazine or benzonitrile [Refs. 2-4], Co^{60} irradiation of a dilute (0.1-1.5%) aqueous solution of benzonitrile [Ref. 5], and lastly, the acid rearrangement of the relatively unavailable polyisocyanides $+C(:NR)+_n$ [Ref. 6].

The major approach investigated for the preparation of poly(organonitriles) under Contract No. N00014-75-C-0991 during the period January-October 1976 [Ref. 7] involved a ring opening polymerization of a halotriazine with subsequent ligand exchange of reactive halogens as shown in Equation (1).

$$(XCN)_3 \xrightarrow{\text{Cat.}} +\underset{X}{C}=N+_n \xrightarrow[-NaX]{RONa} +\underset{OR}{C}=N+_n \qquad (1)$$
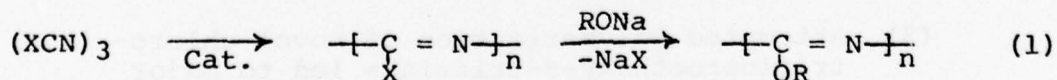
where X equals Cl, Br, and 1-2 halogen atoms
in monomer may be replaced by a monovalent
organic radical R.

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Preparation of $+(Cl)C=N+_n$ is claimed to have been prepared from cyanuric chloride by catalytic polymerization at $\geq 300°C$ [Ref. 8] or by Co^{60} irradiation in the solid state [Refs. 9, 10]. However, both these methods do not readily lend themselves to routine preparation of research quantities of polymer.

The synthetic scheme in Equation (1) is analogous to one used for the preparation of poly(organophosphazene) (phosphorus-nitrogen polymers) plastics and elastomers of structure $[(RO)(R'O)PN]_n$ (where R may be identical to R') from the cyclic monomer $(Cl_2PN)_3$. Horizons has conducted successful work on poly(organophosphazenes) for many years and this work has included fundamental polymerization studies, extensive synthesis, characterization, structure-property relationship studies, compounding and crosslinking, and determination of physico-mechanical properties of the vulcanizates [Refs. 11-18]. All this experience is expected to transfer over to poly(organonitrile) technology. Thus a large variety of polymers should be derivable from $[ClCN]_n$ polymer or derivatives thereof.

Work described in the earlier Technical Report [Ref. 7] under Contract N00014-75-C-0991 is summarized below:

(1) Attempts to polymerize $(ClCN)_3$ catalytically in solution or with radiation in the solid state were unsuccessful. A variety of catalysts such as $(CH_3SO_3Hg)_2O$, CH_3SO_3H, $TiCl_4$, KBF_4, 4-phenylpyridine, CF_3SO_3Na/4-phenylpyridine were tried at 205-208°C.

(2) Attempted polymerization of novel bromo-chloro-s-triazine mixture in polychlorinated benzene solvents led, at best, to low yields of product with very low solution viscosity. Pyridine, triphenylphosphorus, CF_3SO_3Ag, $(C_2H_5)_2AlCl$ in addition to most of the above were screened for catalytic activity at 230-235°C. Significant sublimation of monomer and/or solvent was a constant problem in trying to achieve high reaction temperatures.

(3) Attempted polymerization of novel chloro-trifluoroethoxy-s-triazines led to major degradation with nucleophilic catalysts (4-phenylpyridine, triphenylphosphorus) or with their onium salts. Tris(trifluoroethoxy)-s-triazine is relatively inert to nucleophiles

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but isomerizes when heated with certain acidic reagents. The chloro-trifluoroethoxy-triazine monomers were readily prepared in good yield by reaction of lithium trifluoroethoxide with $(ClCN)_3$.

(4) 2,4-Dichloro-6-phenyl-s-triazine did not polymerize in bulk with either acidic or basic catalyst at 235°C.

Attempted polymerization of bromo-chloro-triazine mixture was also studied from November 1976 to February 1977, but this work will be discussed in Section 3.1.

An alternate approach to the preparation of poly(organonitriles), $+(RO)C=N+_n$, from readily available material is shown in Equation (2):

$$n \ ROC \equiv N \ \xrightarrow{cat.} \ +\underset{OR}{\overset{}{C}}=N+_n \qquad (2)$$

$$(I)$$
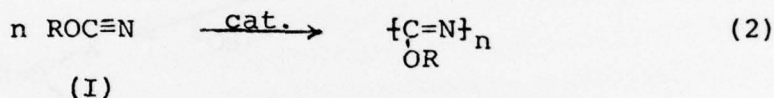
The cyanates (I) are known materials and are readily prepared [Ref. 19] by reaction of cyanogen chloride and an alcohol (or phenol) using a tertiary amine as acid acceptor as shown in Equation (3):

$$Cl-C \equiv N + ROH \ \xrightarrow[-HCl]{R'_3N} \ I \qquad (3)$$
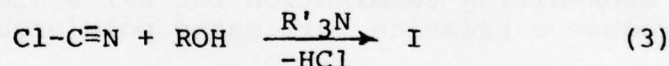
In order to develop poly(organonitrile) technology to its fullest potential, two important conditions must be attainable; i.e., molecular weight control and molecular structure control. One approach to control structure, other than copolymerization, is to exchange organic ligands as shown in Equation (4):

$$\left[\underset{OAr}{\overset{}{C}} = N\right] + CF_3CH_2ONa \longrightarrow \left[\underset{OCH_2CF_3}{\overset{}{C}} = N\right] + ArONa \qquad (4)$$
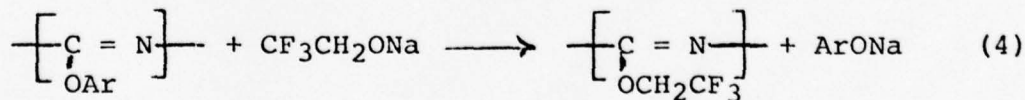
This type of exchange is known for both aryloxy substituted s-triazines [Ref. 20] and phosphazenes [Ref. 21].

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One major problem in the attempted polymerization of organic cyanates, such as phenyl cyanate, is the ease of cyclic trimerization to afford a 2,4,6-trisubstituted-s-triazine. The trimerization of phenyl cyanate by mineral acids, Lewis acids ($AlCl_3$, $ZnCl_2$), and bases (CH_3ONa, CH_3CO_2Na, $(Bu)_3P$, $(C_2H_5)_3N$) has been reported [Refs. 19, 22, 23]. Potential termination side reactions due to trimerization and nitrile formation, at least by anionic initiation, are shown in Equation (5).

$$\text{(5)}$$
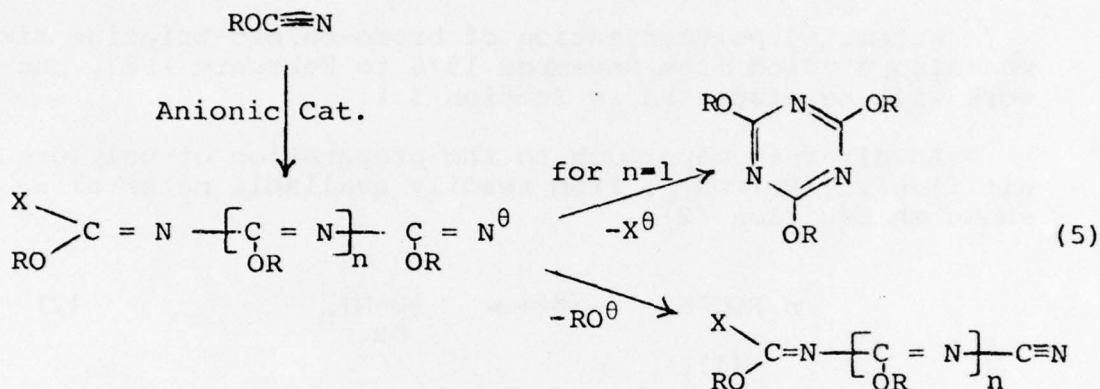
where X is derived from catalyst X^{θ} and may be identical to RO^{θ}

A back-biting termination for n>1 would generate RO^{θ} and produce a triazine terminated poly(organonitrile).

It appeared possible that a study of monomer and catalyst structure and polymerization conditions could identify reaction variables which would optimize the linear polymerization reaction. Therefore, the major part of work on this program was devoted to the preparation of several known cyanates and attempts to polymerize them.

3.0   RESULTS AND DISCUSSION

3.1   Attempted Polymerization of Trihalotriazines

Highlights of this phase are:

(1)   Further attempts to control sublimation in the nucleophilic polymerization of bromo-chloro-triazine mixtures were unsuccessful using phosphorus halides, polyhaloheterocycles, a perfluorinated tertiary amine, and mixtures thereof.

(2)   Attempted polymerization of bromo-chloro-triazine mixture with potassium thiocyanate led to formation of a highly colored, largely insoluble solid.

(3)   Attempted sealed tube polymerization led to tube explosion.

The attempted polymerization of a bromo-chloro-triazine mixture with pyridine catalyst (1% on triazines) was studied. This mixture which is rich in 2,4-dibromo-6-chloro-s-triazine and contains significant amounts of mono-bromo-dichloro-triazine and tribromotriazine was prepared from $(ClCN)_3$ and PBr_3 as described earlier [Ref. 7]. Pentachlorobenzene (ca. 40% of reaction mixture) was used as major solvent and selected materials were screened as minor solvent (ca. 10% of reaction mixture) for sublimation control. Oil bath temperatures of about 235°C were employed. Minor solvents tested and found ineffective for sublimation control were PBr_3, $POBr_3$ (generated Br_2) perfluoro(tri-n-butylamine)(PTBA), 1,3,5-trichlorobenzene with/without (w/wo) PTBA, 2,4-dichloropyrimidine-w/wo-PTBA, 1,1-difluoro-1,2,2,3,3,3-hexachloropropane-w/wo-2,4,6-trichloropyrimidine, 2,4-dichloropyrimidine-2,4,6-trichloropyrimidine, 2,4-dichloro-6-hexafluoroisopropoxy-s-triazine-w/wo-PTBA. One observation appeared particularly noteworthy. Significant viscosity increase was observed 1 hour after $POBr_3$ had been added to a run which had previously been heated 22 hours with PBr_3. This phenomenon is not understood at this time. The resulting product (13% yield) was insoluble in N-methylpyrrolidinone.

Hexakis(thiocyanato)cyclotriphosphazene is reported [Refs. 24, 25] to polymerize at about 150°C, whereas the hexachloro analog $(Cl_2PN)_3$ requires temperatures of about 250°C. Since potassium thiocyanate was found to be a catalyst

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for the solution polymerization of $(Cl_2PN)_3$ [Ref. 26], it seemed appropriate to examine it as a catalyst for halotriazine polymerization. Polymerization was attempted with KNCS (20 wt. % on monomer) using pentachlorobenzene-1,3,5-trichlorobenzene (4w/1w) solvent. The mixture was prereacted, hopefully to effect ligand exchange, 6 hours at 190°C followed by heating 1 day in a bath at 235°C. The reaction progressively darkened, evolved Br_2, and produced a gas chromatographic component after pentachlorobenzene. A brown solid, presumably admixed with potassium salts and free of triazine and solvent, was isolated. Extraction with N-methylpyrrolidinone led to swelling and partial solubilization. Reaction of the extracted products with sodium trifluoroethoxide gave solids which did not melt to 300°C and which showed no significant infrared absorption.

An attempted vacuum sealed tube polymerization of halotriazine mixture in pentachlorobenzene (50%) solvent with pyridine (3% on triazine) catalyst led to bursting of the tube after about 26 hours in a bath at 250°C.

3.2 Attempted Preparation of Poly(organonitriles) Via Organic Cyanates

Highlights of this phase are:

(1) Preparation of research quantities of pure CF_3CH_2OCN has been unsuccessful. Its formation and purification is complicated by addition of CF_3CH_2OH to desired product, and/or trimerization to triazine, and possibly rearrangement to isocyanate.

(2) The relatively stable aryl cyanates (X-ArOCN) where X=H, $2-CH_3$, $2,6-di-CH_3$ were easily prepared in good yields. The 2-chlorophenyl and 2,4-dichlorophenyl cyanates were obtained in poorer yields.

(3) The reactivity of aryl cyanates to anionic catalysts is strongly dependent upon aryl structure, catalyst, temperature, and the presence of solvent. 2-Chlorophenyl cyanate appears to be the most reactive cyanate studied.

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(4) Polymerization of 2-chlorophenyl cyanate generally affords varying amounts of amorphous solid and oil whereas polymerization of 2-cresyl cyanate affords varying amounts of crystalline and amorphous solids. Product distribution in both instances is dependent upon catalyst, temperature, and solvent.

(5) The major hydrocarbon-insoluble fraction obtained from 2-chlorophenyl or 2-cresyl cyanate appears to be very low molecular weight linear polymer.

(6) A poly(aryloxynitrile) easily underwent ligand exchange with trifluoroethoxide to afford poly(organonitrile) copolymer.

3.2.1 Trifluoroethyl Cyanate

2,2,2-Trifluoroethyl cyanate was initially chosen for study. Preparation from BrCN and trifluoroethanol using a tertiary amine acid acceptor was unsuccessful. This is in marked contrast to results obtained using ClCN starting material [Ref. 19].

The preparation of CF_3CH_2OCN was also attempted as shown in Equation (6)

$$CF_3CH_2OM + BrCN \xrightarrow[-MBr]{THF} CF_3CH_2OCN \qquad (6)$$

$$M = Na, Li$$
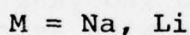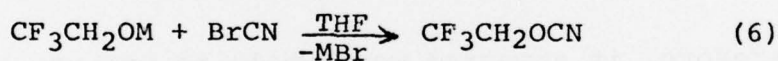
Addition of sodium trifluoroethoxide to cyanogen bromide in tetrahydrofuran (THF) at -20°C was very rapid initially but then greatly decelerated. Subsequent addition of $(C_2H_5)_4N^{\oplus}Br^{\ominus}$ assisted further reaction but did not lead to complete reaction of BrCN. Attempted isolation of product was accompanied by formation of a new lower boiling component. This product may be isocyanate produced by acid (via BrCN) catalyzed rearrangement of CF_3CH_2OCN. Addition of a small amount of water to the organic mixture greatly accelerates this reaction. In one run cyclic trimer, 2,4,6-tris(trifluoroethoxy)-s-triazine, was obtained as a distillation residue. Gas chromatographic analysis showed that this triazine was not formed during the reaction

proper. Use of lithium trifluoroethoxide or $LiOH-CF_3CH_2OH$ led to rapid substitution at $\leq 20°C$. A clear distillable product was obtained. Elemental and infrared analyses confirmed the structure as $(CF_3CH_2O)_2C = NH$. Calculated for $C_5H_5F_6NO_2$: C, 26.6%; H, 2.2%; N, 6.2%. Found: C, 26.2%; H, 2.4%; N, 6.5%.

The formation of $(CF_3CH_2O)_2C = NH$ may occur in one of two ways as shown in Equation (7):

$$BrC\equiv N \nearrow \begin{array}{c} X \\ \overset{|}{BrC=N^\ominus} \end{array} \qquad \qquad$$

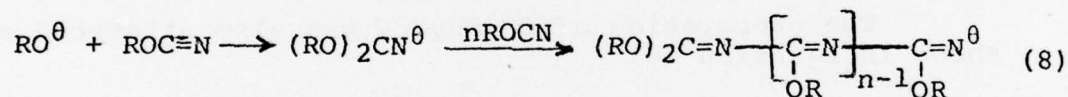$$BrC\equiv N \underset{X^\ominus}{\searrow} X-C\equiv N \qquad \xrightarrow[\text{H source}]{X^\ominus \quad \text{then}} (X)_2C=NH \qquad (7)$$
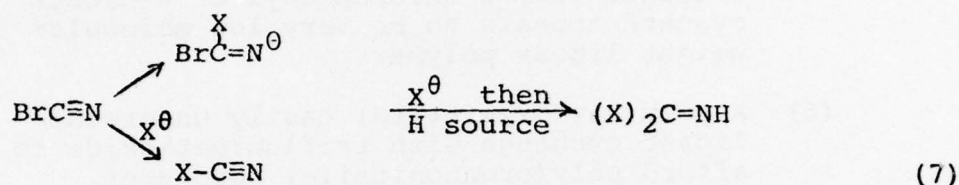
$$\text{where } X = CF_3CH_2O$$

Formation of by-product by base catalyzed addition of CF_3CH_2OH to CF_3CH_2OCN leads one to hypothesize that in the absence of chain termination an anionic polymerization could produce a poly(organonitrile) as shown in Equation (8):

$$RO^\ominus + ROC\equiv N \longrightarrow (RO)_2CN^\ominus \xrightarrow{nROCN} (RO)_2C=N-\left[\underset{OR}{\overset{|}{C=N}}\right]_{n-1}-\underset{OR}{\overset{|}{C=N^\ominus}} \qquad (8)$$

Therefore, it appeared worthwhile to prepare the stabler (to heat and rearrangement to isocyanates) aryl cyanates and to study their polymerization with anionic catalysts.

3.2.2 Aryl Cyanates

It was anticipated that the steric requirements for trimerization and linear polyaddition of cyanates would differ. This type of effect on reaction path has been reported [Ref. 27] for the preparation of aryl cyanates from sterically hindered o-substituted phenols and cyanogen chloride. Imidocarbonates [$(RO)_2C=NH$] or triazines were not produced, unlike the case when unhindered phenols or aliphatic alcohols were used. Another reason why steric hindrance might be important is that ligand exchange by catalyst on $-(ArO)C=N-$ sites would be less likely to occur if the catalyst were hindered. Therefore, a polyaddition reaction to linear polymer
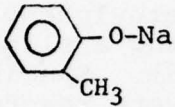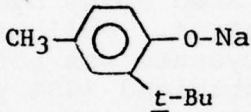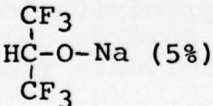
could occur by proper selection of monomer and/or catalyst. To check this hypothesis, aryl cyanates differing in steric requirements near the cyanate function were prepared and their reactivity to nucleophiles differing in steric configuration as well as basicity was investigated. Organometallic compounds of tin and lead were also studied because several of these compounds were reported [Ref. 28] to lead to polymerization of dinitriles.

Phenyl, 2-cresyl and 2,6-dimethylphenyl cyanates were prepared in good yields (45-78%) using a slightly modified procedure of the literature [Ref. 19]. Specifically, cyanogen bromide and the appropriate phenol were reacted at low temperatures in the presence of a tertiary amine and solvent. Product was isolated by removal of precipitated amine hydrobromide, water washing, drying, and distillation. Following the same procedure purified 2-chlorophenyl cyanate was not obtained. However, workable quantities were obtained (33% yield) by replacing the methylene chloride solvent with acetone as originally described [Ref. 19]. 2,4-Dichlorophenyl cyanate was obtained in lower yield and was contaminated with 2,4-dichlorophenol.

Unless stated otherwise, all attempted cyanate polymerizations were run without solvent and employed 2% catalyst (by weight on monomer). Polymerizations were carried out in serum capped vials containing a magnetic stirring bar. Catalyst solutions were introduced using a hypodermic needle. Elevated temperatures discussed in this section refer to oil bath temperatures. Products from homogeneous runs were generally isolated by diluting the reaction mixture with a small amount of benzene followed by precipitation with petroleum ether or cyclohexane. The more soluble product fraction was obtained by removal of solvents from the precipitation liquor.

2-Cresyl cyanate rather than phenyl cyanate was employed in initial screening studies because the cresyl derivative showed better shelf life. The results are shown in Table I. The importance of catalyst structure and polymerization conditions on product composition is clearly evident. Three different solids can be formed, an amorphous solid melting somewhere in the range 45-65°C, an unknown white crystalline solid m.p. 101-103°C, and trimer m.p. 158-159°C.

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TABLE I

ATTEMPTED POLYMERIZATION OF 2-CRESYL CYANATE

Run[a]	Catalyst	Remarks
1	(benzene ring with O–Na and CH₃)	Significant quantity of white needles formed.
2	(benzene ring with CH₃, O–Na, and t-Bu)	Significant viscosity increase; 12% yield solid m.p. 50–65°C.
3[b]	"	29% yield m.p. 45–50°C.
4	"	Very viscous after 4 hours @ 55°C, 5% yield amorphous solid after 1 day.
5	" (0.5%)	31% yield trimer after 1 week.
6	" (2% Li⊕ salt)	30% yield m.p. 85–100°C after 6 days.
7	$\begin{array}{c}CF_3\\|\\HC-O-Na \ (5\%)\\|\\CF_3\end{array}$	No effect.
8	$(C_6H_5)_3P$	No effect (even after overnight at 110°C).
9	$(C_2H_5)_3N$	30% yield trimer after 7 days.
10	$(C_4H_9)_2Sn(OCH_3)_2$	34% yield m.p. 99–103°C after 6 days.
11	"	51% yield m.p. 101–103°C after 1 hr. at 55°C.

(a) Unless indicated otherwise, polymerizations were run on neat monomer (2–2.4 g) at room temperature approximately 1 day using 2% catalyst.

(b) Employed 4.8 g monomer. Run became very hot and viscous shortly after introduction of catalyst. See Example 3 of Appendix I for details.

The product isolated from the polymerization (Run 2, Table I) of 2-cresyl cyanate and sodium-2-t-butyl-4-cresyloxide (SBCO) was a yellow solid m.p. 50-65°C, which showed infrared (IR) absorptions at 4.5μ (possibly conjugated -CN) and 6.1μ (conjugated -C≡N-) [see Figure 7], and unlike starting material showed no gas chromatographic response. In contrast, the known cyclic trimer 2,4,6-tris(2-cresyloxy)-s-triazine is white, melts at 158-159°C, and has no IR absorptions at 4.5μ and 6.1μ [See Figure 4]. Product structure is discussed in Section 3.3.

A brief study was made to determine the effects of solvent polarity on the polymerization of 2-cresyl cyanate. The polar N,N-dimethylacetamide (DMAc) and non-polar n-heptane were employed with SBCO catalyst. No obvious reaction (via gas chromatographic analysis) was observed after several days at room temperature with DMAc solvent, whereas heptane afforded two immiscible layers in which white crystals predominated in the lower layer. Other catalysts studied (several days, R.T.) in heptane and DMAc were sodium-2-cresyloxide (SCO), tetrabutyl lead, dibutyl tin dimethoxide, and copper acetylacetonate. Little or no reaction was observed in DMAc regardless of catalyst. In heptane the heavy metal catalysts led to formation of white needles, but SCO was without effect. The white solid isolated using the tin catalyst was the same product isolated in neat runs (10 and 11 of Table I). It melted at 101-103°C and showed IR absorptions at 4.5μ and 6.1μ [see Figure 5].

Phenyl cyanate, the least hindered aryl cyanate, was briefly studied and found to be an unviable candidate for production of poly(organonitrile). SBCO gave a low yield of white crystalline solid m.p. 153-156°C after 1 day at R.T. but led to a low yield of crude trimer at 55°C. Infrared of the solid m.p. 153-156°C showed strong absorption at 4.5μ and 6.1μ and was very similar to the solid m.p. 101- 103°C isolated by reaction of 2-cresyl cyanate with tin catalysts. Reaction of phenyl cyanate at R.T. with the tin compounds (Bu)$_2$Sn(OCH$_3$)$_2$, stannous octoate, and (Bu)$_2$SnO led to extensive formation of white crystals.

The results with 2-cresyl cyanate and phenyl cyanate indicate that steric hindrance at the cyanate function by an ortho substituent affects product composition and might favor a linear polyaddition reaction instead of trimerization to triazine. The variances in physical state and melting points of products from 2-cresyl cyanate possibly reflect different degrees of polymerization and/or different modes

of termination. To further test the hindrance concept the polymerization of 2-chlorophenyl cyanate was undertaken. Mechanistically it was anticipated that the electron withdrawing effect of the Cl group would make the cyanate more reactive to anionic initiation.

The results of polymerizations with 2-chlorophenyl cyanate are shown in Table II. Unless indicated otherwise two product fractions were isolated, a lightly colored cyclohexane insoluble amorphous solid melting over a range of 5° to 10°C somewhere around 45° to 61°C and a relatively colorless viscous oil. IR of the amorphous solid showed the characteristic absorptions at 4.5μ and 6.1μ [see Figure 8] observed with the amorphous product derived from 2-cresyl cyanate. Runs giving good yields of amorphous solid were generally red viscous solutions prior to workup.

Several conclusions can be drawn from these results, namely:

(a)   With the exception of the very basic tris-amino phenolic catalyst [Run 12] hindered phenoxide salts give approximately similar results.

(b)   Use of solvent [Run 3] dramatically alters the course of reaction.

(c)   Change of cation [Run 4] from Na to quaternary ammonium leads to inactivity.

(d)   Use of salts derived from carbon acids (i.e. compounds with an acidic -CH site) leads to relative inactivity [Run 13] or dramatic change in product [Run 14].

(e)   Reaction time, at least at 85°C, appears to effect product composition [Runs 8, 9].

The results with 2-cresyl and 2-chloro cyanates suggested investigating the effects of greater hindrance and greater electron-withdrawal at the cyanate site. To this end 2,6-dimethylphenyl and 2,4-dichlorophenyl cyanates were prepared. The dimethyl monomer was checked with sodium 2-t-butyl-4-cresyloxide (2%) at 55°C (24 hours) with and without diglyme solvent and neat with sodium 2,3,5,6-tetramethylphenoxide (24 hrs., 55°C). The neat run with SBCO gave a 28% yield of white solid m.p. 133-135°C and a 33% yield of oil which showed IR absorptions at 4.5μ and 6.1μ. IR of

TABLE II

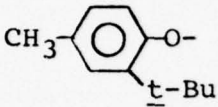### ATTEMPTED POLYMERIZATION OF 2-CHLOROPHENYL CYANATE
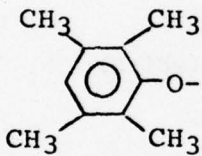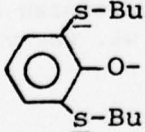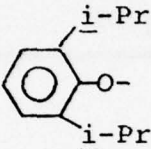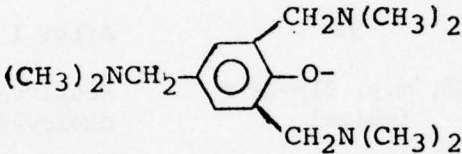
Run [a]	Catalyst, Na Salt of HX, X=	% Yield Amorphous Solid [b]	Remarks
1	CH₃—〈ring〉—O⁻ with t-Bu	58	
2	"	58	After 1 week at R.T.
3	"	31, m.p. 218–22°C (white)	Equal volume diglyme employed.
4	"	None	Benzyl trimethyl ammonium salt was employed.
5	CH₃,CH₃—〈ring〉—O⁻ with CH₃,CH₃	50	After 24 hours at R.T.
6	"	56	
7	"	62 [n_{rel}=1.03; mol. wt. = 360]	
8	"	33; also 19 m.p. 170–172°C (white), [n_{rel}=1.01]	Thick deep red grease with suspended solids after 24 hrs. at 85°C.
9	" (1 or 2%)	50–58 [n_{rel}=1.01]	After 5 hours at 85°C.
10	s-Bu—〈ring〉—O⁻ with s-Bu	54 (gum)	

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TABLE II (continued)
ATTEMPTED POLYMERIZATION OF 2-CHLOROPHENYL CYANATE

Run [a]	Catalyst, Na Salt of HX, X=	% Yield Amorphous Solid [b]	Remarks
11	i-Pr–[C6H3]–O– (2,6-di-i-Pr)	40 [n_{rel}=1.01]	
12	(CH3)2NCH2–[C6H2]–O– with CH2N(CH3)2 groups	81 (white)	Set up hard.
13	$(C_2H_5O\overset{O}{\overset{\|}{C}})_2\overset{|}{\underset{H}{C}}-$	9, m.p. 65–75°C (white)	
14	$(CN)(t\text{-}BuO\overset{O}{\overset{\|}{C}})\overset{|}{\underset{H}{C}}-$	65, m.p. 135–145°C	Reaction full of fine solids.

(a) Unless indicated otherwise, polymerizations were run neat at 55°C (oil bath) for 24 hours using 2% sodium salt catalyst.

(b) Relative solution viscosities were run in tetrahydrofuran at 30.5°C using a concentration of 0.1 g/10 ml. Molecular wt. was via vapor phase osmometry in acetone.

the crystalline product was similar to the white crystalline
solid m.p. 101°C derived from 2-cresyl cyanate. The solvent
based run and tetramethylphenoxide run showed inactivity.
2,4-Dichlorophenyl cyanate was screened with sodium 2,3,5,6-
tetramethylphenoxide at 55°C (24 hours). A small amount of
diglyme (0.5 ml per 4 g cyanate) was employed to liquefy the
solid monomer. Three product fractions were isolated, a
benzene-cyclohexane insoluble solid (11%) m.p. 40°-50°C, a
cyclohexane-petroleum ether insoluble solid (5%) m.p. 60-70°C
and a high yield of gum which contained no starting material.
There was insufficient time to permit further characterization.

Lastly to rule out the possibility of a radical
initiated polymerization 2-chlorophenyl cyanate was heated
with α,α'-azobisisobutyronitrile (2%) for 20 hours at 75°C.
This resulted in triazine and unreacted monomer.

3.3 Product Structure

As discussed earlier, several products result from the
anionic catalyzed polymerization of aryl cyanates. Structure
assignment of the white crystalline solids will be discussed
first because they are either known compounds or molecularly
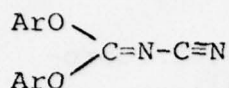simple species.

Trimers, that is 2,4,6-tris(aryloxy)-s-triazines, were
isolated from phenyl, 2-cresyl and 2-chlorophenyl cyanates.
Their melting points are shown in the upper half of Table III.

Structure assignment of the 2-chloro product m.p. 170-
172°C is based on the strong similarity of its IR spectrum
[See Figure 6] with the two known triazines. The 2-chloro
product was obtained by polymerization (Run 8 of Table II)
as well as from distillation of monomer (forerun, rich in
2-chlorophenol, led upon standing to deposition of white
crystalline solid).

The unknown white crystalline solids isolated from the
aryl cyanates are shown in the bottom half of Table III.
Infrared spectra are very similar, all showing strong
absorptions at 4.5μ and 6.1-6.15μ. The corresponding
triazines do not show absorption in either of these regions.
These unknown solids might be aryl cyanate dimers. A dimer
structure (II) could result by catalyst (X^θ) addition to aryl
cyanate, followed by loss of aryloxide anion to give III, and
subsequent exchange of X by aryloxide anion. The last step
of this sequence might be favored because of possible relief
of strain due to steric hindrance in the intermediate III.

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TABLE III

WHITE SOLIDS ISOLATED FROM ARYL CYANATE POLYMERIZATIONS

X =	Melting Point (°C) [Ref. 20]	Melting Point Observed (°C)
H	234.5-236	232-234
2-CH$_3$	159 -160	158-159
2-Cl	---	170-172

[X-ArOCN]$_n$ X =	Unknown Crystalline Solid m.p. (°C)
H	153-156
2-CH$_3$	101-103
2-Cl	---
2,6-diCH$_3$	133-135

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$$\begin{matrix} ArO \\ ArO \end{matrix} \Big\backslash C=N-C\equiv N \qquad\qquad \begin{matrix} X \\ ArO \end{matrix} \Big\backslash C=N-C\equiv N$$
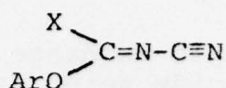
II   III   (X = hindered aryl-
                                              oxy radical)

Structure II is consistent with strong IR absorptions observed
at 4.5µ (conjugated nitrile) and 6.1µ(C=N).

   The amorphous solids with approximate melting point
45-60°C isolated from 2-cresyl and 2-chlorophenyl cyanates,
respectively, are believed to be low molecular weight linear
poly(aryloxy nitriles), $\{(ArO)C=N\}_n$, where n is a small
integer. The consistent appearance of one or two absorption
bands at 4.5-4.6µ in the infrared suggest that the polymer
may be terminated with nitrile as in structure II above.
Therefore, a probable polymer structure can be represented
by structure IV

$$ArO \Bigg[\begin{matrix} C=N \\ | \\ OAr \end{matrix} \Bigg]_n C\equiv N$$
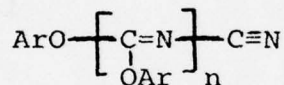
IV

The formation of IV as shown in Scheme 1 would be similar to
the proposed formation of II except that the polyaddition
reaction has occurred to a greater extent. Structure IV is
consistent with:

   (a)   The observed elemental analyses [see examples
         3 and 4 of the Appendix].

   (b)   The IR absorptions at 4.5µ-4.6µ (C≡N) and
         6.1µ (C=N). [See Figures 7 and 8 and compare
         with Figure 1-4 and 6.]

   (c)   Differences in physical form and melting point
         would be expected for product containing dif-
         ferent degrees of polymerization.

   (d)   NMR spectrum is completely different from
         monomer or triazine NMR spectra [see Figures
         10 to 12].

(e) A rapid exchange reaction with trifluoro-
ethoxide anion [see Section 3.4].

The above observations are inconsistent with a triazine termi-
nated polymer. With respect to the IR absorptions, the new
absorptions at 4.5μ and at about 6.1μ when dinitriles were
polymerized were both assigned to conjugated -C=N- bonds
[Ref. 28]. In addition, polymerization of 2,4,6-(RO)3-s-triazines
gave products which showed an infrared absorption, assigned
to -C=N-, at 6.1μ [Ref. 2].

Initiation: $X^{\ominus} + ArOC\equiv N \longrightarrow$

$$X\diagdown_{ArO}C=N^{\ominus}$$

Propagation:

$$\begin{array}{c} X \\ \diagdown \\ ArO \end{array}C=N^{\ominus} + nArOCN \longrightarrow X\left[\begin{array}{c}C=N \\ | \\ O \\ | \\ Ar\end{array}\right]_n \begin{array}{c}C=N^{\ominus} \\ | \\ O \\ | \\ Ar\end{array}$$

Termination:

$$X\left[\begin{array}{c}C=N \\ | \\ O \\ | \\ Ar\end{array}\right]_n \begin{array}{c}C=N^{\ominus} \\ | \\ O \\ | \\ Ar\end{array} \longrightarrow X\left[\begin{array}{c}C=N \\ | \\ O \\ | \\ Ar\end{array}\right]_n C\equiv N + ArO^{\ominus}$$

Exchange:

$$\begin{array}{c}X \\ \diagdown \\ ArO \end{array}C=N\left[\begin{array}{c}C=N \\ | \\ O \\ | \\ Ar\end{array}\right]_{n-1} C\equiv N \xrightarrow[-X^{\ominus}]{} ArO\left[\begin{array}{c}C=N \\ | \\ O \\ | \\ Ar\end{array}\right]_n C\equiv N$$

$O^{\ominus}$
Ar
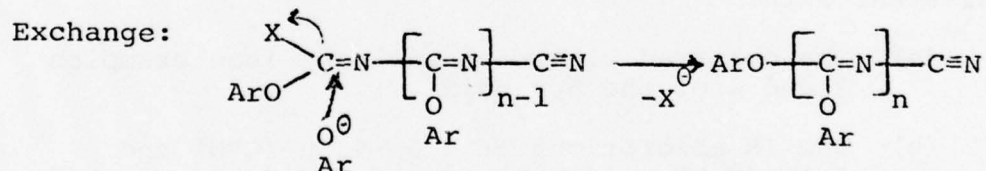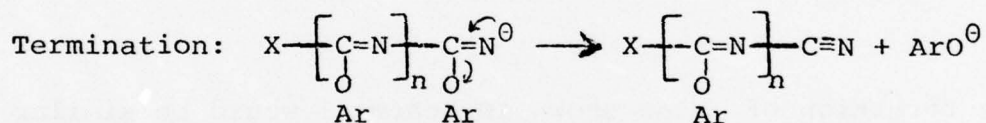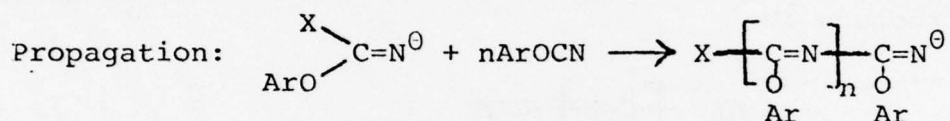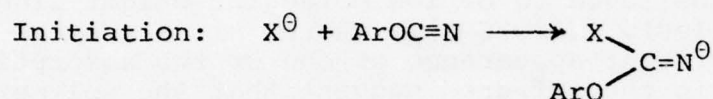
where $X^{\ominus}$ = hindered aryloxide anion
Ar = hindered aryl radical

SCHEME 1

PROPOSED ANIONIC POLYMERIZATION MECHANISM OF
ARYL CYANATES

3.4 Substitution Reactions of Poly(organonitriles)

An attractive feature of poly(aryloxynitrile) chemistry is their potential to be transformed into other poly(organo-nitriles) as shown in Equation (4) of Section 2.0. To check this capability the amorphous (m.p. 45-50°C) and crystalline (m.p. 101-103°C) fractions obtained by polymerization of 2-cresyl cyanate were reacted at room temperature with a solution of sodium trifluoroethoxide in tetrahydrofuran. Aliquots were removed with time, acidified, and analyzed gas chromatographically. In both instances 2-cresol was produced quickly in significant quantity, highly suggestive of the desired ligand interchange. This ligand exchange reaction was successfully performed using the amorphous solid (m.p. 46-53°C) obtained by polymerization of 2-chlorophenyl cyanate [Run 6 of Table II]. A good yield of an orange colored gum, presumed to be copolymer, was obtained. Elemental fluorine analysis was indicative of approximately 80% exchange. This material, unlike 2,4,6-tris(trifluoroethoxy)-s-triazine, did not show volatile component(s) via gas chromatographic analysis (240°C). Infrared analysis [Figure 9] showed an absorption at 8.55μ characteristic of a CF_3 group and proton NMR spectrum [Figure 13] showed new strong absorptions at 4.5-5 ppm. The ligand exchange of solid m.p. 170-172°C isolated from polymerization of 2-chlorophenyl cyanate [Run 8 of Table II] also rapidly exchanged with trifluoroethoxide. In conclusion, ligand exchange of poly(aryloxynitriles) appears to be extremely facile.

4.0 RECOMMENDATIONS

1. Continue study of the anionic polymerization of 2-chlorophenyl cyanate using increasingly hindered aryloxide salt catalysts. Investigate effects of catalyst concentration and polymerization temperature on product composition and molecular weight.

2. Study polymerization of other potentially inexpensive aryl cyanates containing an electron-withdrawing group in the ortho position.

3. Determine thermal and hydrolytic stability of poly(organonitriles).

4. Prepare poly(trifluoroethoxy-nitrile) from poly(aryloxynitrile) and study its thermal and hydrolytic stability. If stability is good determine applicability as nonflammable fluid.

EXPERIMENTAL EXAMPLES

Example 1.   Preparation of 2-Cresyl Cyanate

Under nitrogen with stirring, 2-cresol (145.8 g,
1.35 mole was added to a solution (-5°C) of cyanogen bromide
(157.2 g, 1.48 mole) in methylene chloride (450 ml) followed
by the addition of triethylamine (136.2 g, 1.35 mole) over a
1-3/4 hour period while maintaining a reaction temperature
of -5° to 0°C.   Stirring was continued for one hour at
temperature.   The reaction mixture was then suction filtered
to remove precipitated amine hydrobromide which was washed
with methylene chloride (50 ml).   After an ice water wash and
drying over anhydrous potassium carbonate, the solvents from
the filtrate were removed at room temperature under house
vacuum to give an orange liquid.   Distillation through a
Vigreaux column (12") gave 96 g of a liquid, b.p. 89°C/12 mm
[literature b.p. 87-90°C/10 mm, [Ref. 19].   Infrared spectrum
[see Figure 1] showed the characteristic -OC≡N absorption at
4.42µ.

Example 2.   Preparation of 2-Chlorophenyl Cyanate

Under nitrogen while stirring, 2-chlorophenol
(115.4 g, 0.898 mole) was added to a solution (-10°C) of
cyanogen bromide (100 g, 0.943 mole) in acetone (375 ml),
followed by the addition of pyridine (71.03 g, 0.898 mole)
over a 3 hour period while maintaining a reaction temperature
of -10°C.   Stirring was continued at temperature for 3 hours.
The reaction was stirred with petroleum ether (1 ℓ) and then
the liquor was decanted from the precipitated pyridine
hydrobromide which was washed with petroleum ether (100 ml).
After an ice water wash and drying over anhydrous sodium
sulfate, the solvents were removed at room temperature
under house vacuum to give an orange liquid.   This liquid
was flash distilled at 62°C/0.3 mm to give a clear distillate
(106 g) which was then redistilled through a Widman column
at 48°C/0.2 mm [Lit. b.p. 64-67°C/0.5 mm, Ref. 19] to give
73 g of clear liquid.   A second distillation through the
Widman column at 48°C/0.15 mm gave 46.9 g of a clear liquid.
The infrared spectrum [see Figure 2] showed the characteris-
tic -OC≡N absorption at 4.42µ. Proton NMR spectrum is shown
in Figure 10.

Example 3. Attempted Polymerization of 2-Cresyl Cyanate

Under nitrogen, a dry flask equipped with a rubber serum stopper was charged with 2-cresyl cyanate (4 g) and 2% by weight of sodium 2-t-butyl-4-cresyloxide (80 mg). The catalyst used was a 15% solution in diglyme which was introduced by means of a hypodermic syringe. After 10 minutes, an exothermic reaction occurred and the contents of the flask became very viscous. The reaction mixture was washed with hexane and then with petroleum ether-benzene (2V/1V). The precipitated orange gum was dissolved in benzene and precipitated with petroleum ether. The product was washed with methanol-water (2V/1V) and vacuum dried to give 1.4 g of material that melted at 45° to 50°C. Elemental analysis calculated for $[C_7H_7OCN]_n$: C, 72.10%; H, 5.25%; N, 10.51%. Found: C, 70.74%; H, 5.52%; N. 10.54%. Infrared spectrum [see Figure 7] showed absorption at 4.51 and 6.1 microns.

The liquor from the above precipitation was evaporated and vacuum dried to give 0.8 g of a yellow gum-like material. The IR spectrum of this material showed many similarities to the IR of the solid product above.

Example 4. Attempted Polymerization of 2-Chlorophenyl Cyanate

Under nitrogen, a dry flask equipped with a rubber serum stopper was charged with 2-chlorophenyl cyanate (2.6 g) and 2% by weight of sodium 2,3,5,6-tetramethyl phenoxide (52 mg). The catalyst was a 15% solution in diglyme. The reaction was heated for 24 hours in an oil bath at 55°C to produce a very thick orange colored material. The contents were dissolved in benzene (3 ml) and precipitated into cyclohexane (15 ml). Upon vacuum drying the precipitate, 1.6 g of a yellow powder was obtained, which melted at 50° to 58°C. The relative viscosity was 1.01 (0.1 g/10 ml THF, 30.5°C) and the molecular weight (vapor phase osmometry, acetone) was 360. Elemental analysis calculated for $[C_6H_4ClOCN]_n$: C, 54.7%; H, 2.6%; Cl, 23.1%. Found: C, 55.8%; H, 3.7%; Cl, 20.0%. Infrared spectrum [see Figure 8] showed absorptions at 4.51 and 6.1 microns. Proton NMR spectrum is shown in Figure 12.

The liquor from the above precipitation was evaporated and vacuum dried to afford 1.1 g of a pale yellow gum. The IR spectrum of this material showed many similarities to the IR of the solid product above.

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Example 5.   Interchange of Poly(2-Chlorophenoxy nitrile)
            with Sodium Trifluoroethoxide

        Sodium trifluoroethoxide (1.7 g, 0.014 mole in
10 ml tetrahydrofuran) was charged under nitrogen with stir-
ring to a flask (0°C) containing the orange solid (1.4 g)
m.p. 46-53°C obtained from Run 6 [see Table II]. The reaction
was stirred at room temperature for 6 hours. Gas chroma-
tographic analysis of aliquots (neutralized with acetic acid)
indicated the reaction to be essentially instantaneous.
2-Chlorophenol content was essentially identical in "0", 1,
and 6 hour samples. The reaction mixture was neutralized
with 1 ml of acetic acid and then extracted with 10 ml of
benzene. Removal of benzene and vacuum drying at 60°C
afforded an orange colored gum (0.75 g). The infrared
spectrum [see Figure 9] was complex and showed a single peak
at 4.6µ (starting material showed a peak at 4.5µ and a strong
shoulder at 4.6µ) in addition to a strong band at 8.55µ
characteristic of $-CF_3$ absorption. Proton NMR spectrum is
shown in Figure 13. The strong appearance of peaks at
4.5-5 ppm is attributed to CF_3CH_2O- protons. Proton
absorptions at 2-2.4, 3.3-3.6, and 7-7.3 ppm are attributed
to $2-ClC_6H_4O-$ (compare with starting material, Figure 12).
Elemental analysis calculated for $[CF_3CH_2OCN]_n$: C, 28.8%;
H, 1.6%; F, 45.6%. Found: C, 37.44%; H, 2.75%; F, 36.5%.
Calculated for 80% replacement of $2-ClC_6H_4O$ by CF_3CH_2O:
C, 33.9%; H, 1.8%; F, 36.5%.

APPENDIX II

INFRARED AND PROTON NUCLEAR MAGNETIC RESONANCE SPECTRA

Infrared spectra were run neat or as Nujol mulls using
a Perkin-Elmer Model 457 infrared spectrophotometer. Proton
NMR spectra were run in $CDCl_3$ solvent using either a Varian
Model EM360A NMR spectrophotometer [Figures 10, 11] or a
JEOL Model JNM-FX600 NMR spectrophotometer [Figures 12, 13].
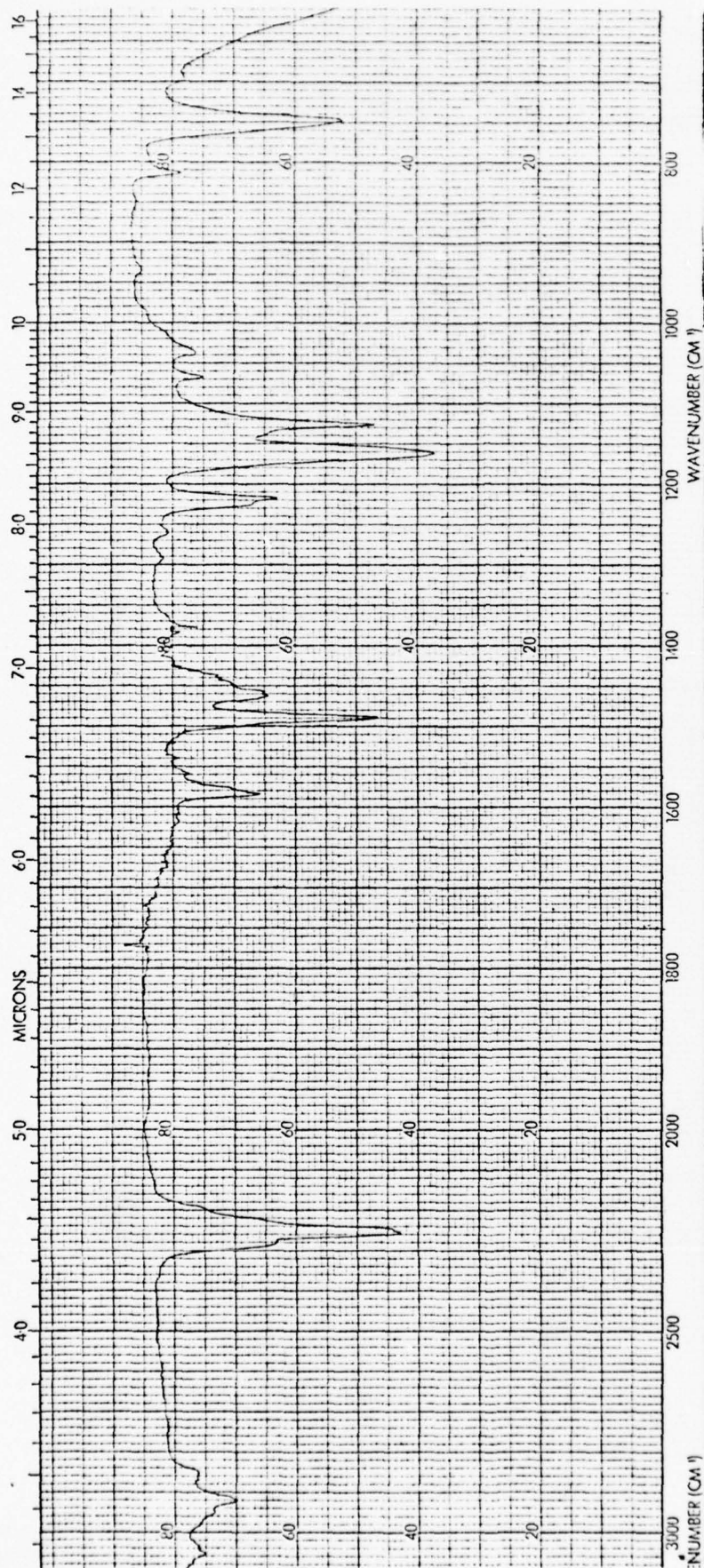Tetramethylsilane was used as reference for the NMR spectra.
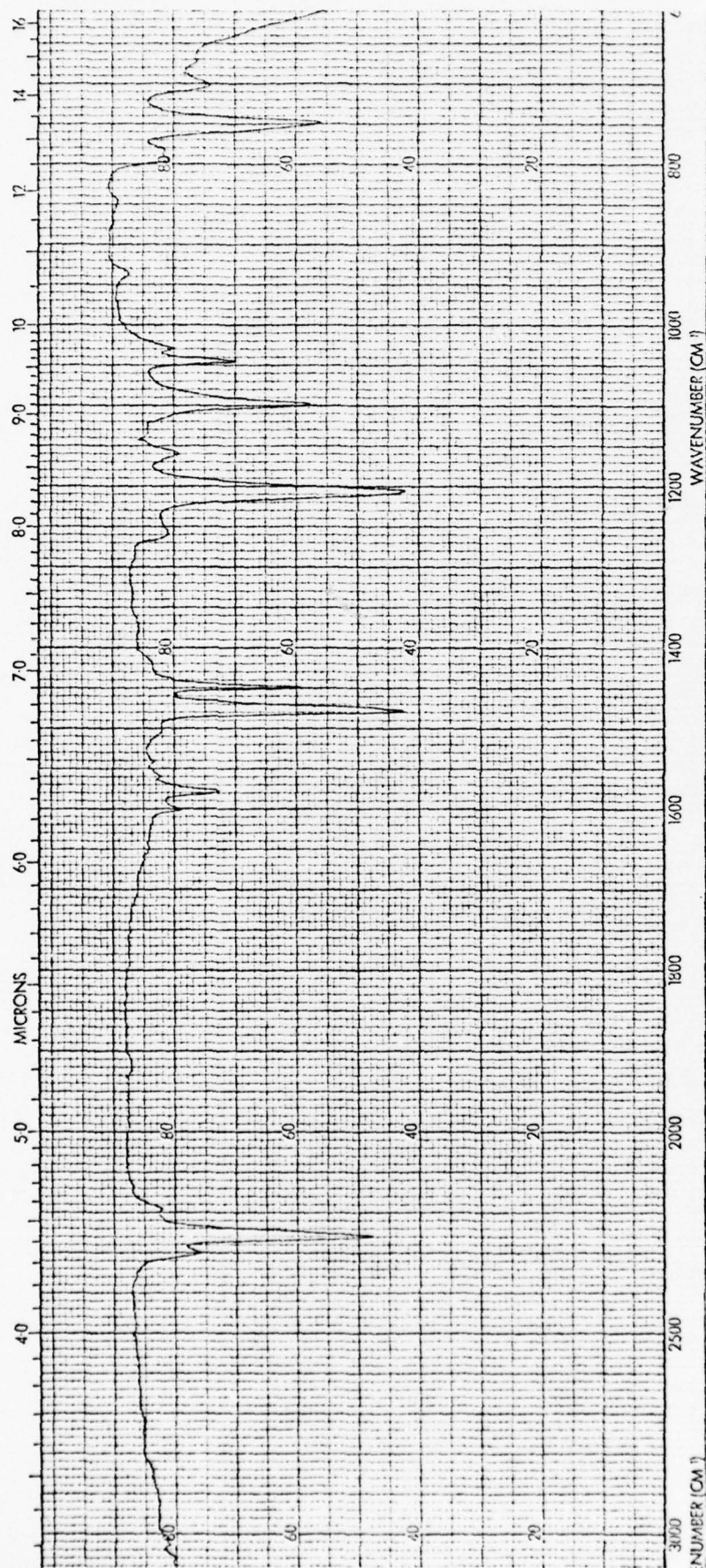
Figure 1. IR Spectrum of 2-Cresyl Cyanate

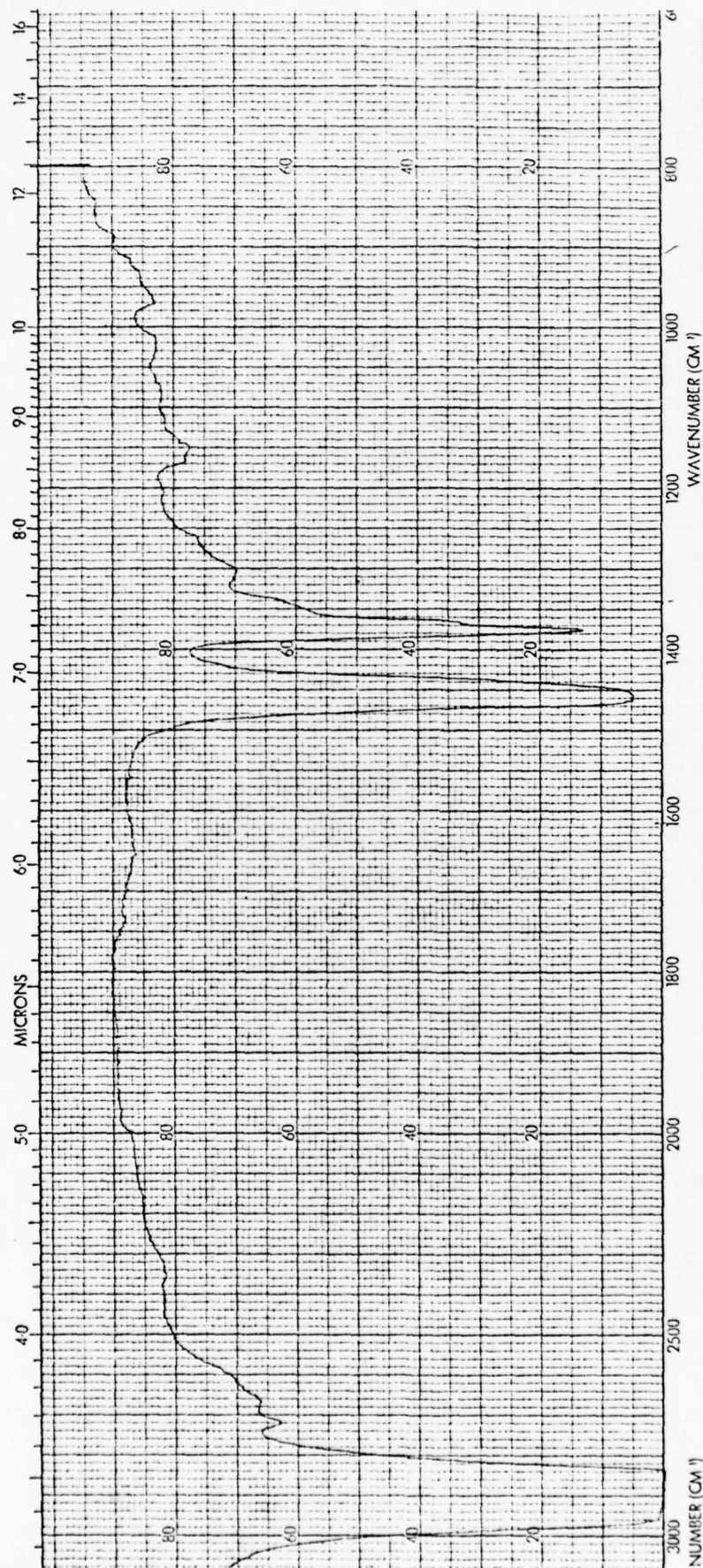Figure 2.   IR Spectrum of 2-Chlorophenyl Cyanate

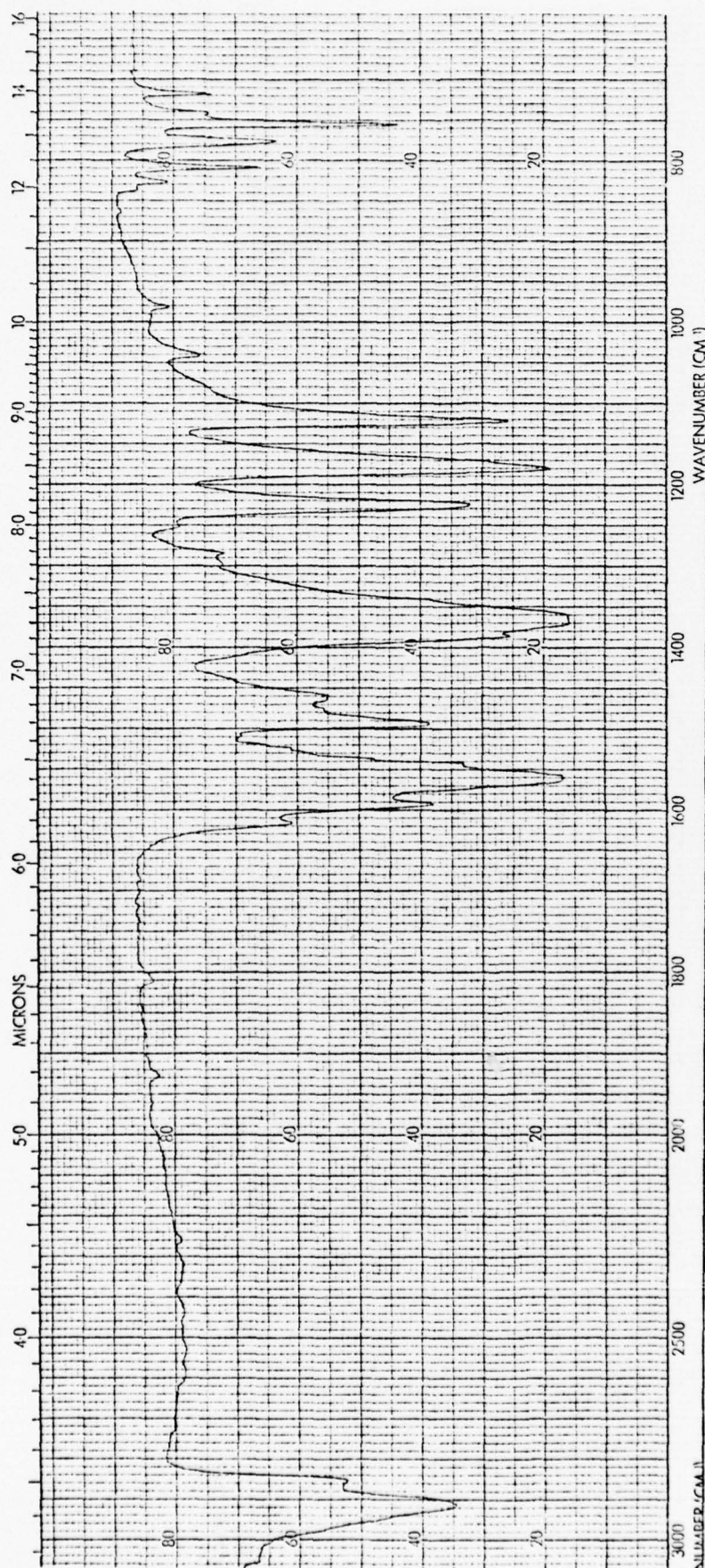Figure 3.   IR Spectrum of Nujol

27

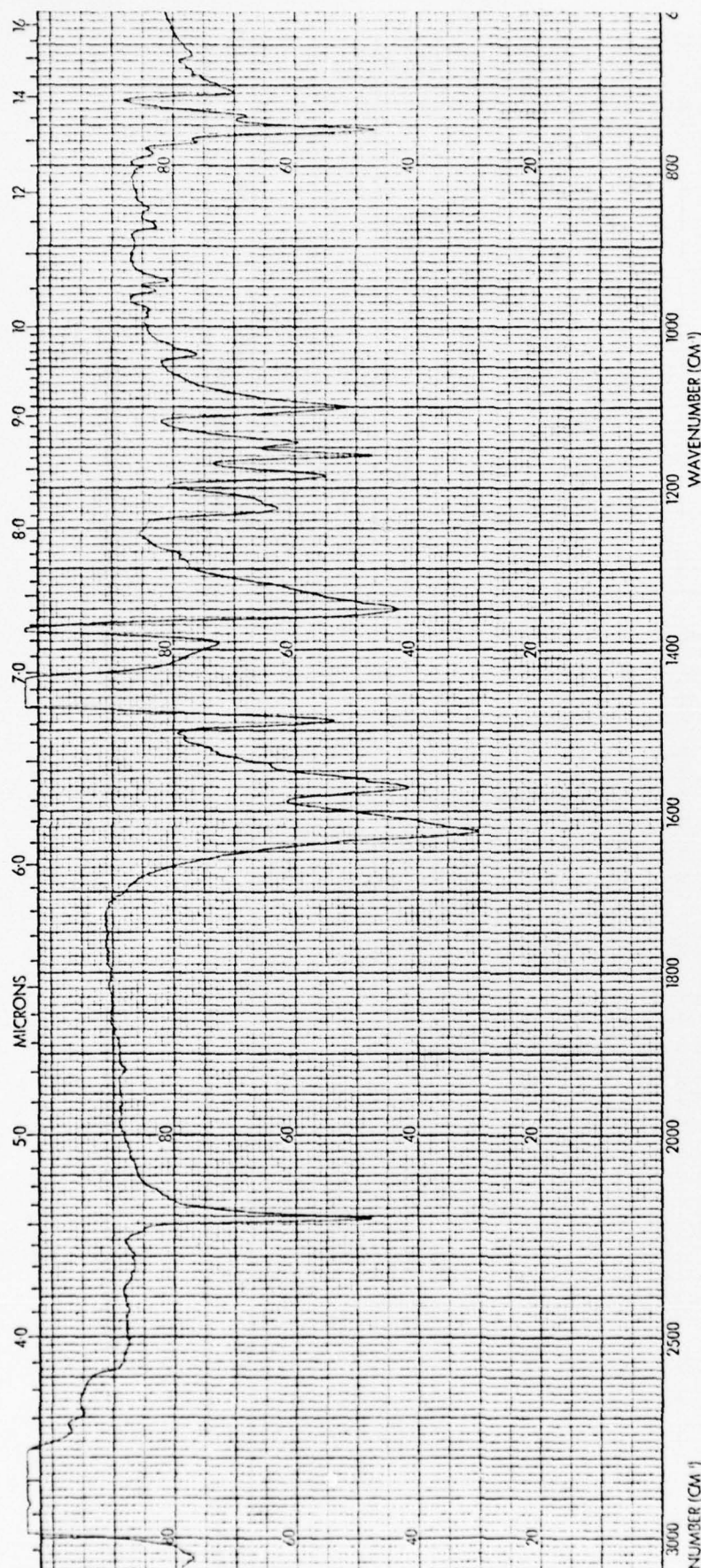Figure 4. IR Spectrum of 2,4,6-Tris(2-cresyloxy)-s-triazine
(Nujol mull)

28

Figure 5. IR Spectrum of Solid M.P. 101–103°C from 2-Cresyl Cyanate
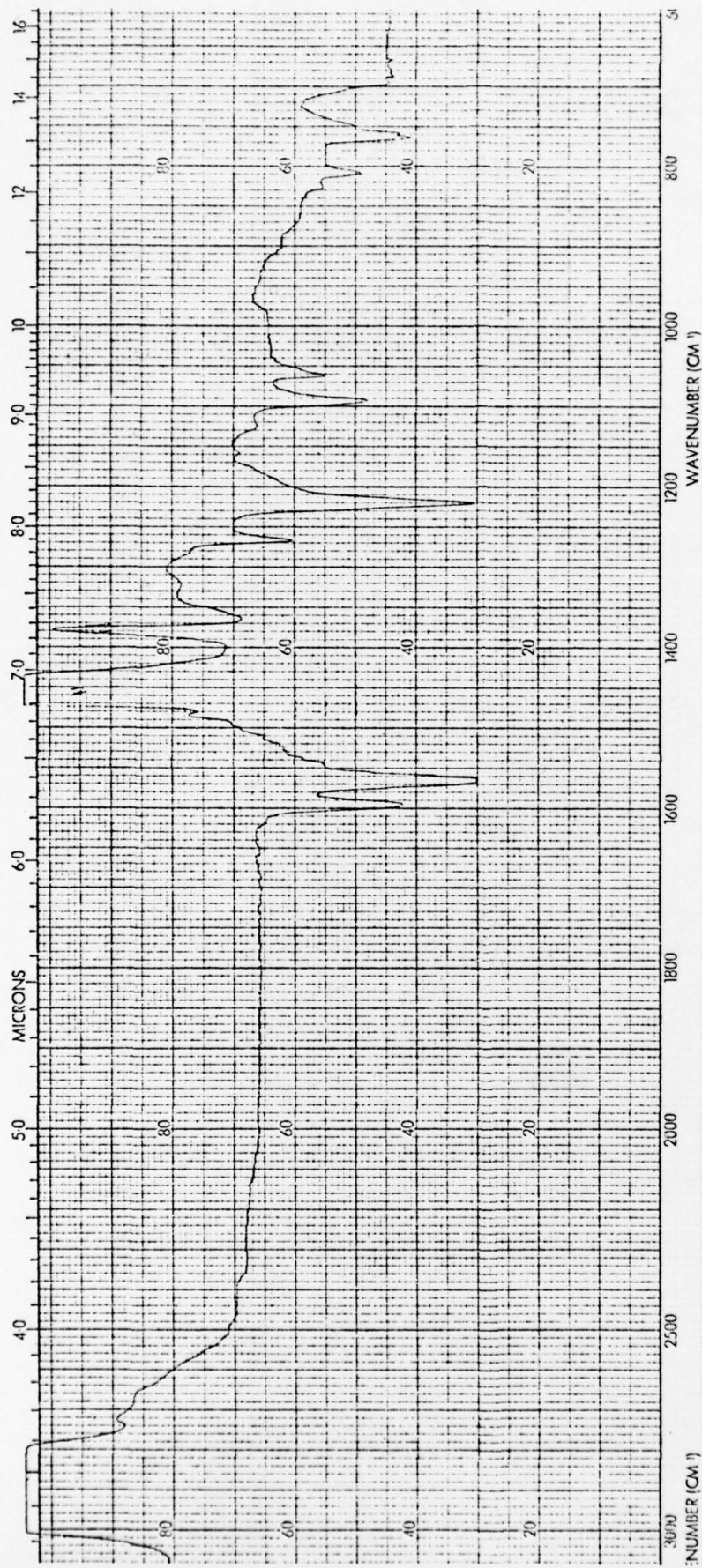(Nujol mull)

29

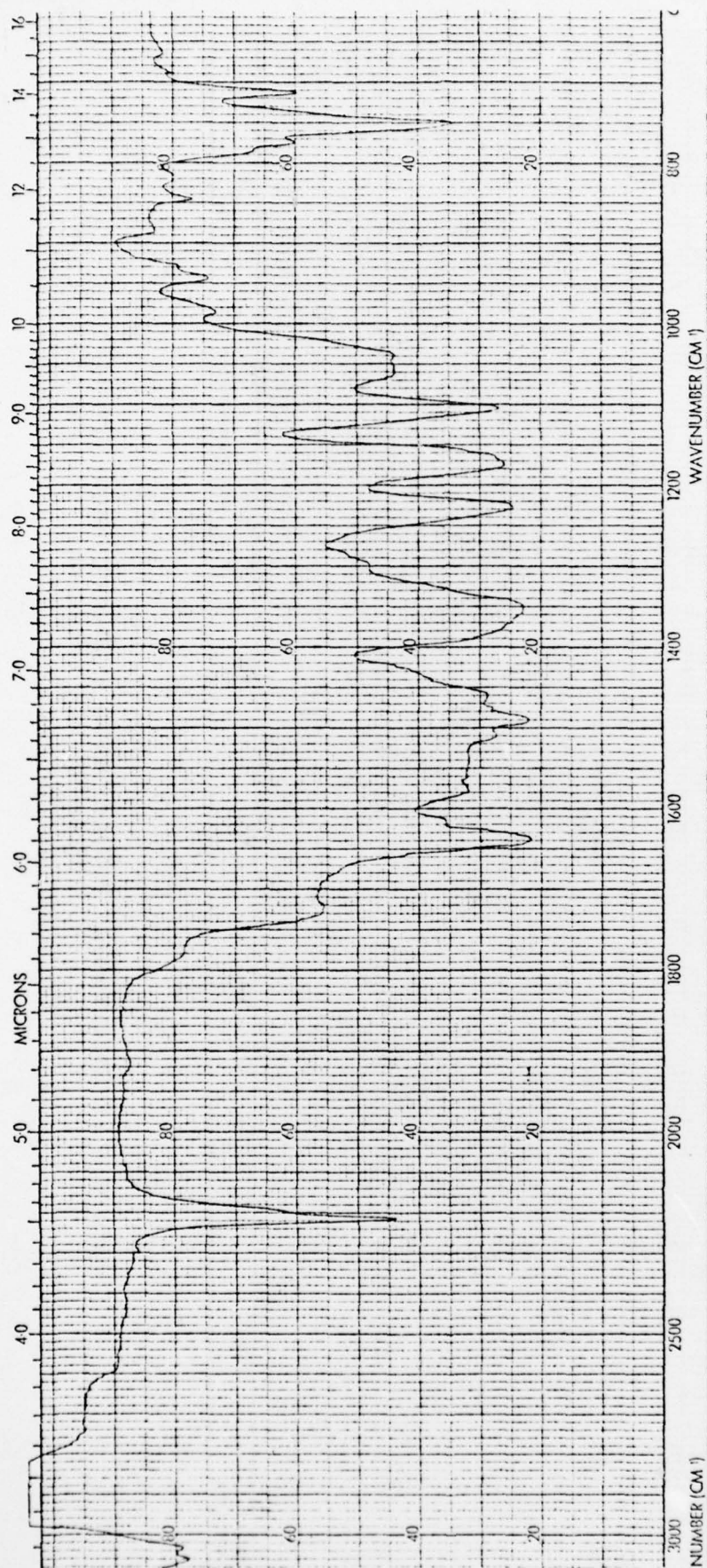Figure 6. IR Spectrum of 2,4,6-Tris(2-chlorophenoxy)-<u>s</u>-triazine (Nujol mull)

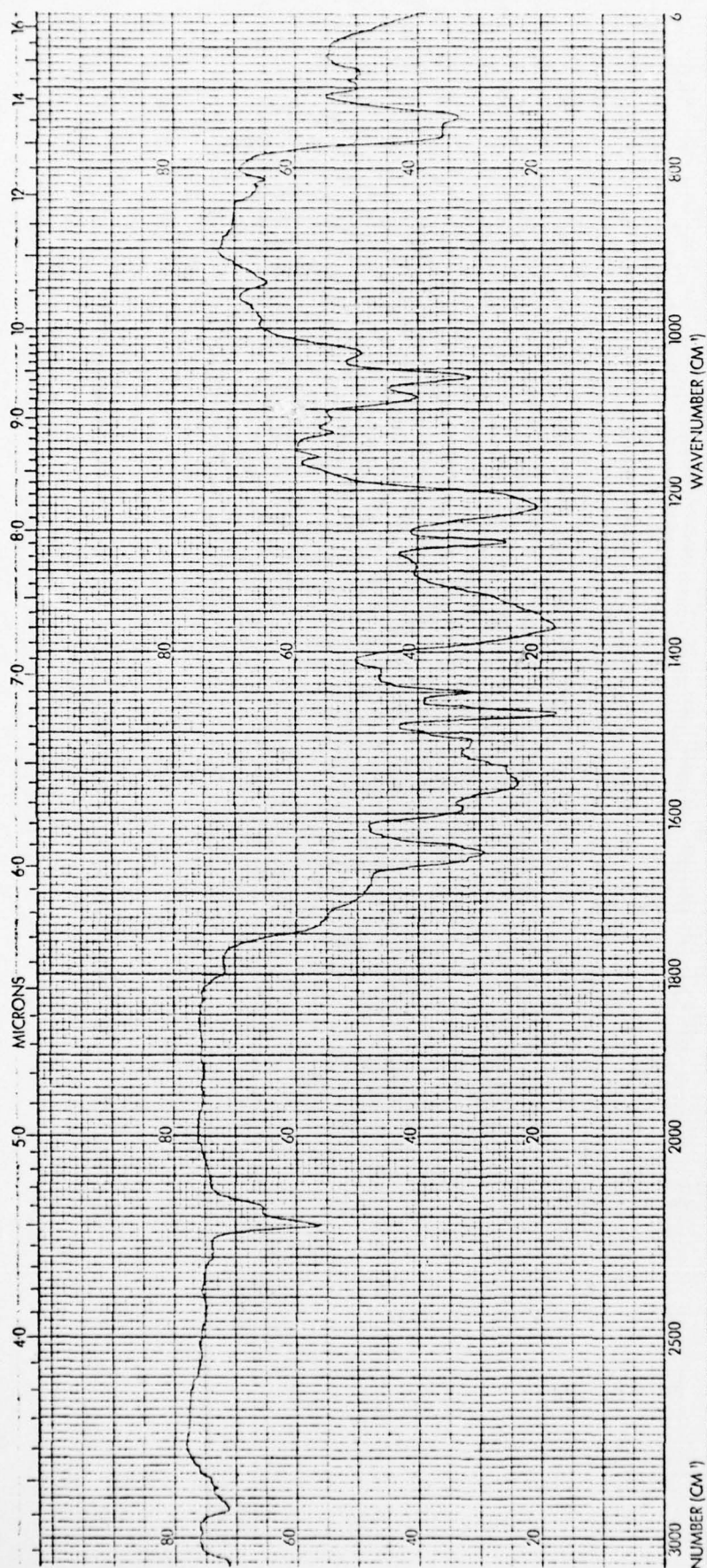Figure 7. IR Spectrum of Polymer from 2-Cresyl Cyanate
(Nujol mull)

31

Figure 8. IR Spectrum of Polymer from 2-Chlorophenyl Cyanate
(from CH_2Cl_2 solution)

32
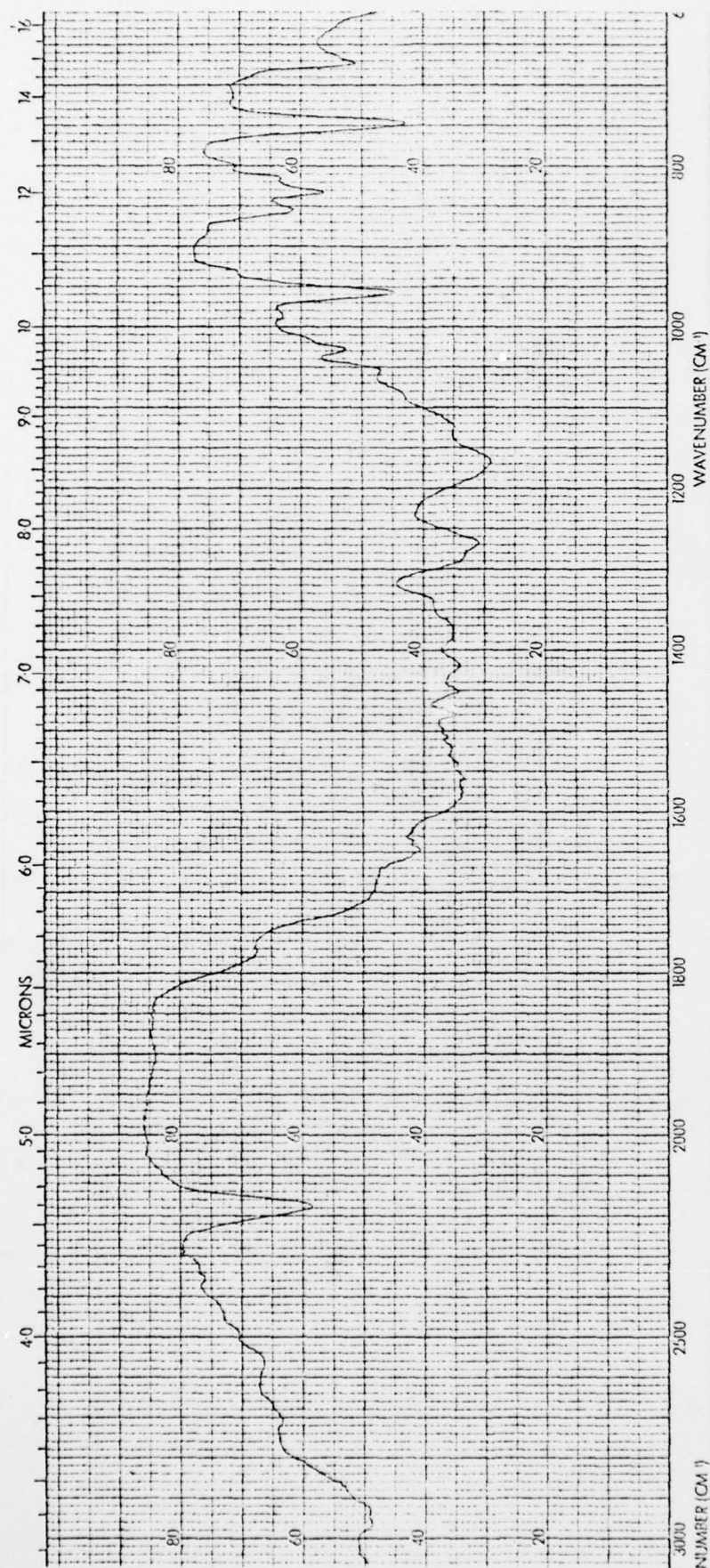
Figure 9. IR Spectrum of Poly(nitrile) Copolymer,
$\{(ClC_6H_4O)C=N\}_x[(CF_3CH_2O)C=N]_y$

33

Figure 10. Proton NMR Spectrum of 2-Chlorophenyl Cyanate

34

Figure 11. Proton NMR Spectrum of 2,4,6-Tris(2-Chlorophenoxy)-s-triazine
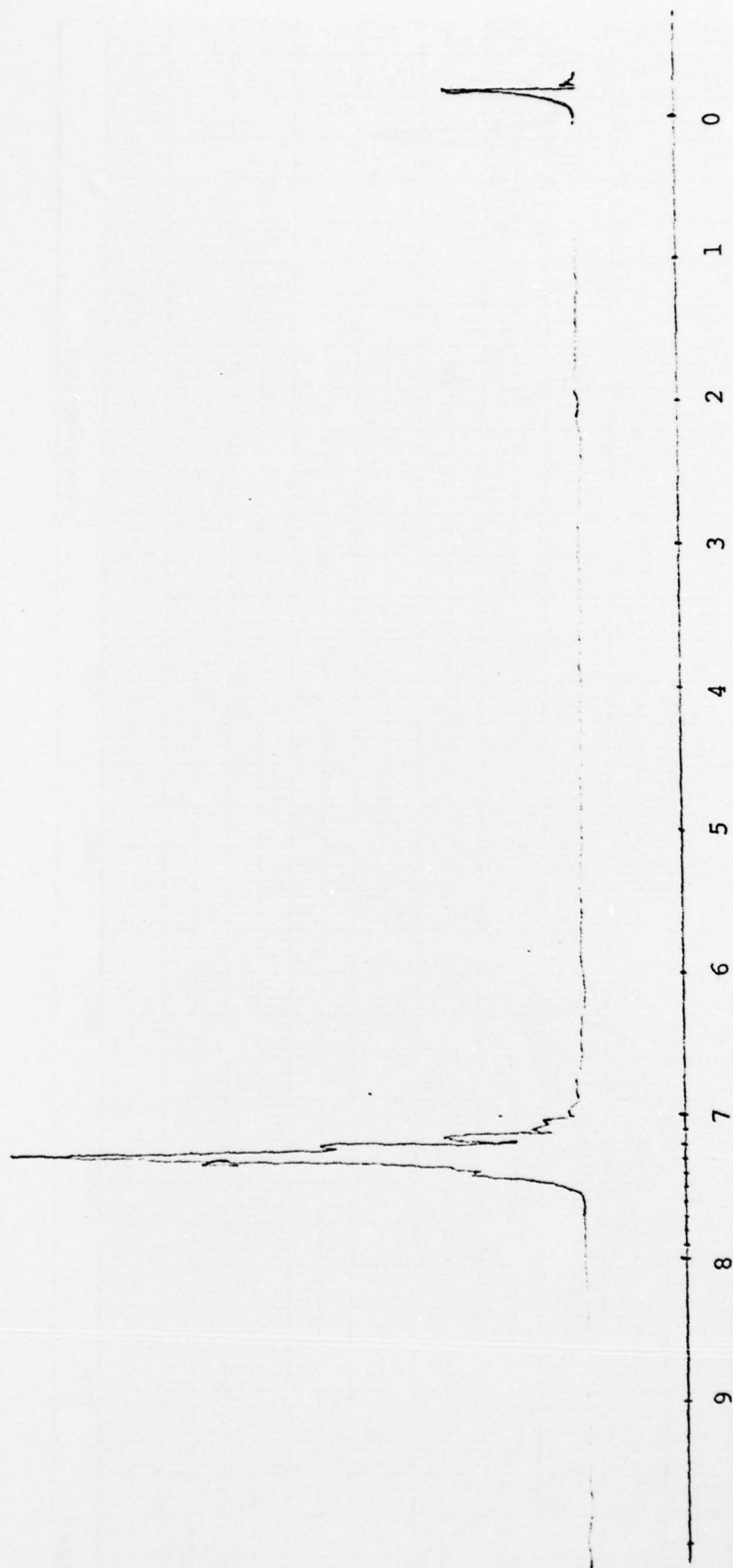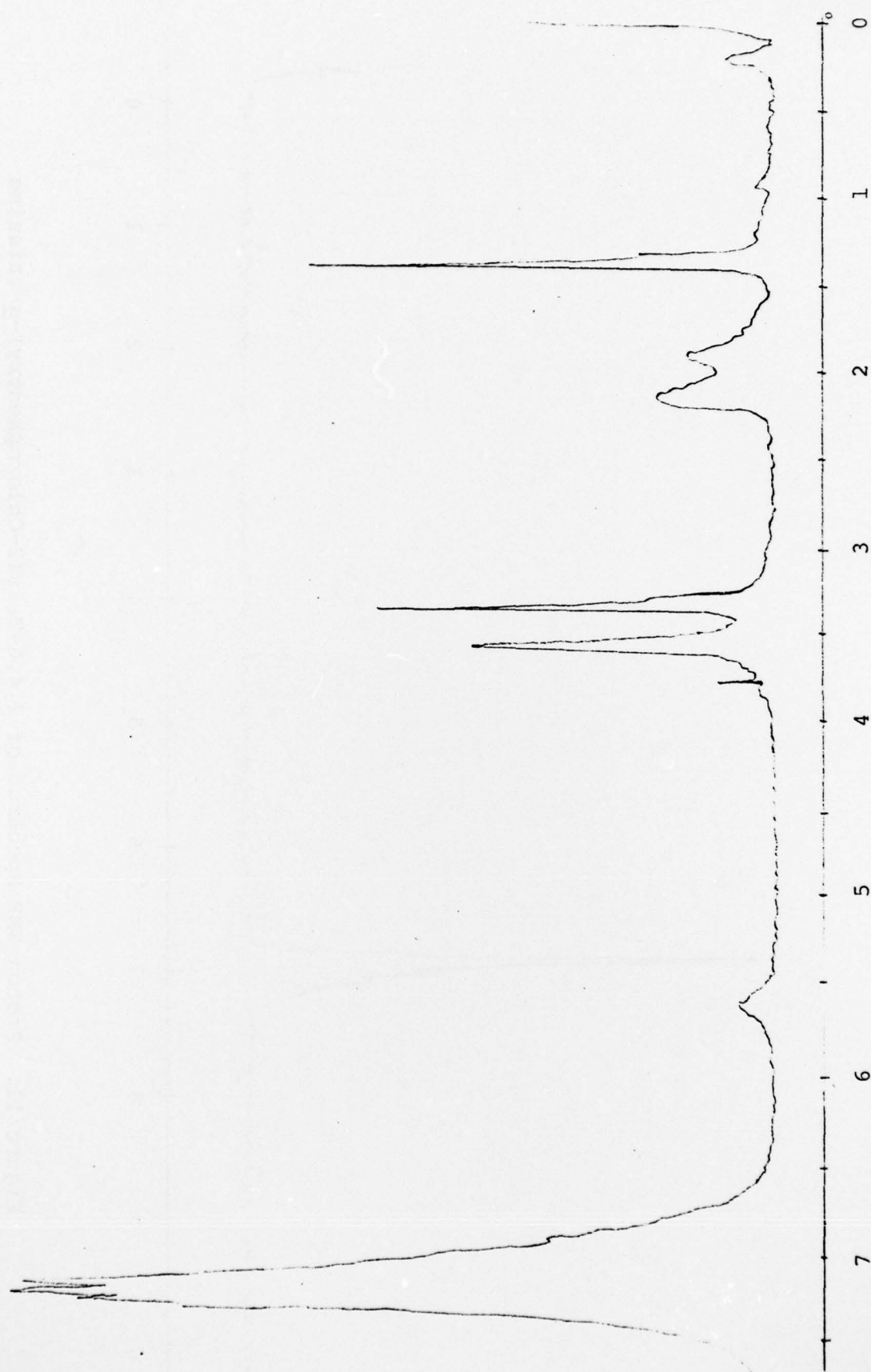
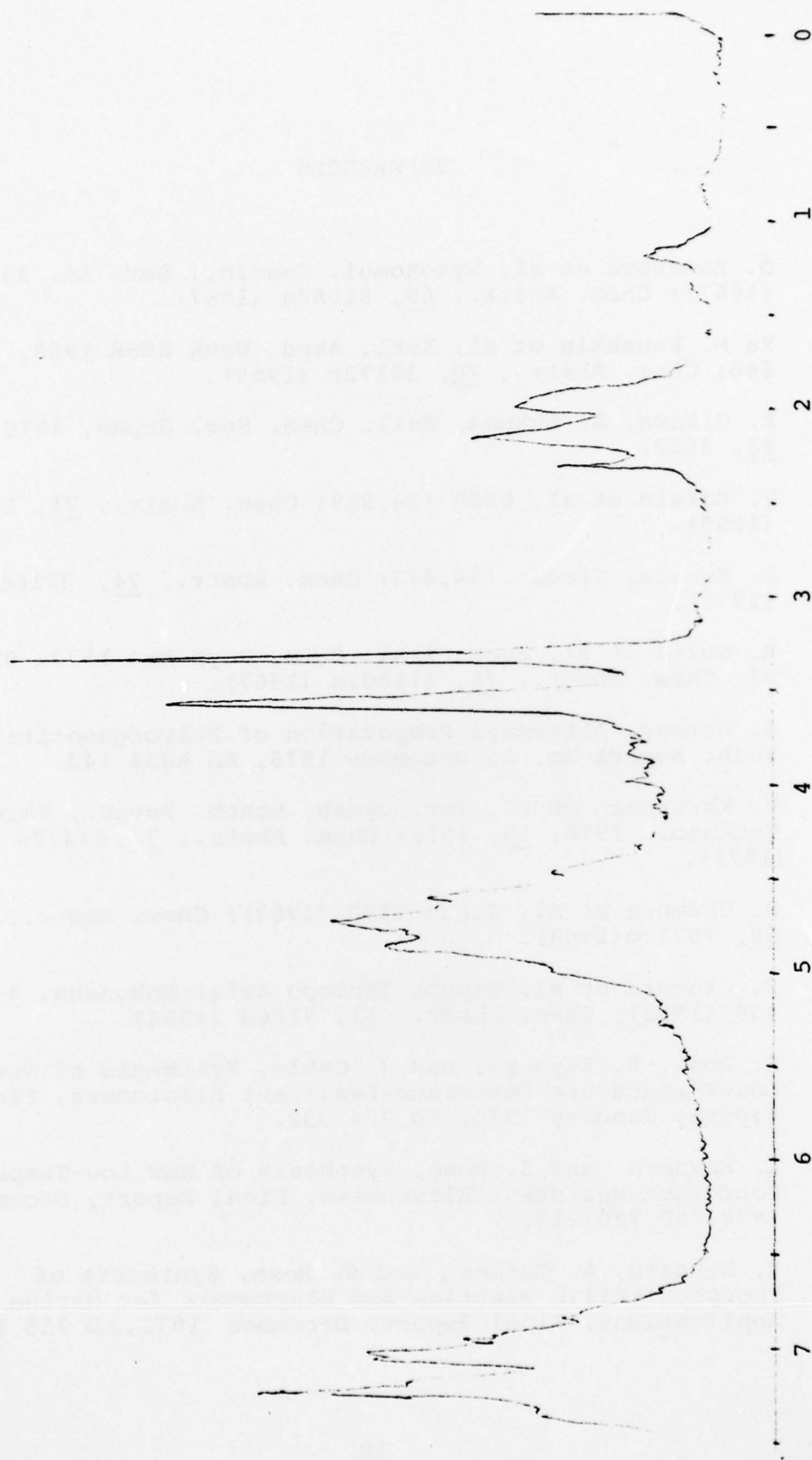Figure 12. Proton NMR Spectrum of Polymer from 2-Chlorophenyl Cyanate

Figure 13. Proton NMR Spectrum of Poly(nitrile) Copolymer, $\{(ClC_6H_4O)C=N\}_x\{(CF_3CH_2O)C=N\}_y$

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